CONTRIBUTIONS FROM THE CHEMICAL LABORATORY
OF HARVARD COLLEGE.

CONCERNING GAS-ANALYSIS BY MEASUREMENT IN CONSTANT VOLUME UNDER CHANGING PRESSURE.

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In Hempel's admirable book upon gas-analysis is described a method of exact analysis which has not received the general attention that it deserves. Instead of measuring the changing volume under constant pressure, he suggested measuring changing pressure in constant volume.[*]

Possibly one reason for the neglect under which this excellent method has suffered is the demand made by it for the use of a large quantity of mercury. One object of this paper is therefore to point out that the same principle may be applied conveniently in a simpler manner.

In Hempel's apparatus the gas to be measured is confined in a bulb immersed in a mercury-trough, and the absorption is effected in an Ettling-Doyère gas-pipette. It is more convenient to measure the gas in a bulb provided with a capillary outlet at the top, and to conduct the absorption in an ordinary Hempel pipette of small size, or in one of the simpler forms of pipette recently used in this laboratory.[†] This manipulation of course introduces the necessity of using rubber connections, which Hempel desired to eliminate; but if they are properly connected[‡] and securely wired, their introduction is not usually a serious defect.

If not more than 25 per cent of the gas is to be absorbed in any one process, a water column of 2.5 meters, easily obtainable in the laboratory, is enough to furnish the necessary change of pressure; hence water may be used as the liquid in the measuring vessel instead of mercury, pro-

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[*] Hempel's Gas-analysis, translated by Dennis, p. 76 (1902), p. 44 (1892) (Macmillan).

[†] Richards, These Proceedings, 37, 273 (1901). Zeitschr. anorg. Chem. 29, 359 (1902).

[‡] Richards, ibid, pages 275 and 362, respectively.

vided of course that none of the components in the gas to be analyzed is
soluble in water.   As will be shown, the use of water greatly simplifies
the measurement of pressure, for an appreciable error in the height of
the column causes no appreciable effect on the result.   Hence no cathe-
tometer is needed, and the simplest apparatus suffices.

Although a marked tube (such as an inverted burette) may be used
for the attainment of constant volume, the measuring apparatus consists
preferably of a bulb of about 50 c.c. capacity with a single mark upon its
stem.*   This bulb should have a capillary tube above with an internal
diameter not far from 1 mm.,† while below it is provided with a straight
tube about 20 cm. long and 7 mm. in diameter, with a sharp line etched
just below the bulb.   To this tube is attached a levelling bulb by means
of a rubber tube about 150 cm. long.‡   The levelling bulb is conveniently
hung from a bent stick, which may be clamped to the iron ring-stand,
either above or below the table-top.   Of course the bulb should be en-
closed in a water-jacket, conveniently made from an inverted broken
bottle, in order to insure constancy of temperature.   The arrangement
is represented in the Figure.

In case the full absorption of 25 per cent is expected, it is conven-
ient, although not necessary, to begin with an excess of pressure.   So
much gas is put into the apparatus for analysis that a pressure of about
a meter of water (measured by means of a wooden meter-rule) is neces-
sary to compress the gas exactly to the mark on the stem.   About 10
per cent (5 c.c.) more gas than the amount needed to fill the space under
atmospheric pressure may be introduced for this purpose.   The height
of this water-column is reduced to the mercury standard at $0°$ by multi-
plying it by about $\frac{1}{13.62}$; § and the reduced value is added to the barometric

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* Mr. W. N. Stull has suggested the use of a tube with several connected bulbs
with as many marks in order to attain a wider range with less change of pressure.
This apparatus will soon be tested in this Laboratory.

† The rubber tube attached to the capillary should be very thick-walled and
have an exceedingly fine bore.   It should be wired to the glass in the manner
shown in the diagram.

‡ In order to prevent the admission of small air-bubbles into the measuring bulb
from the long rubber tube, a trap may be formed by bending the lower glass tube
through $100°$, or else by making a loop in the rubber tube in the fashion shown in
the diagram.   This precaution is very rarely necessary, however; it is much better
to be certain in the first place that no such air-bubbles are present.

§ The divisors corresponding to various temperatures of water column are as
follows : —

$10°$ Divisor $= 13.60$		$20°$ Divisor $= 13.62$	
$15°$ „ $= 13.61$		$25°$ „ $= 13.63$	
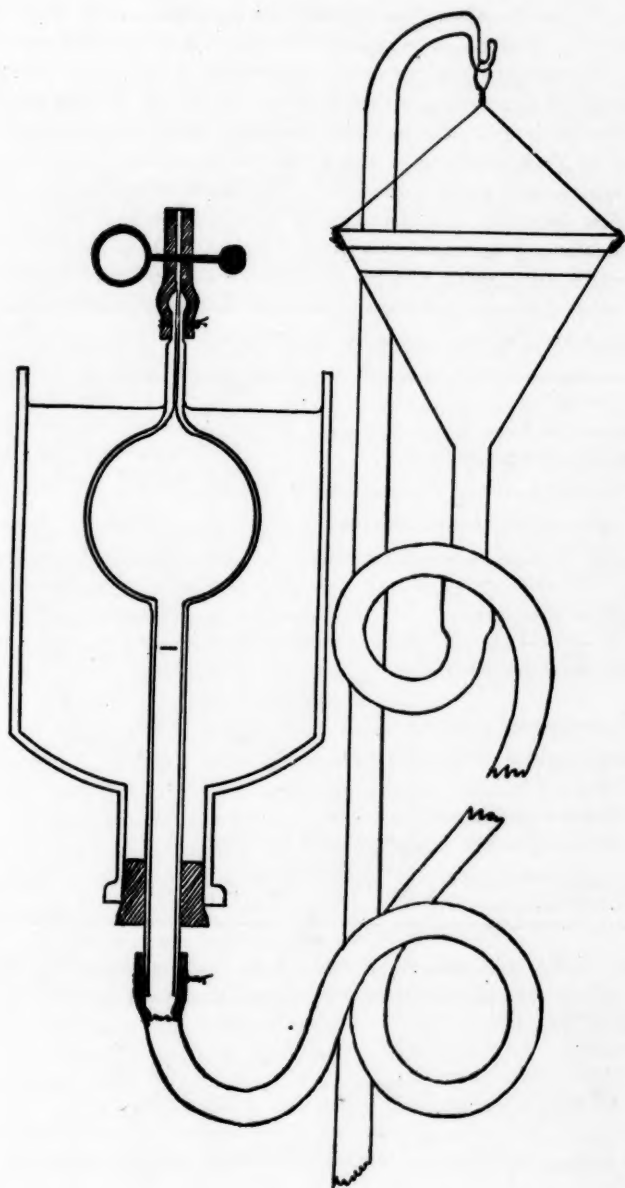
height. After the absorption of one of the components a lower pressure is needed to effect the same adjustment. The loss of pressure gives the means of computing the percentage composition of the gas. Of course the tension of aqueous vapor should be subtracted from the *total* readings since the gas is moist; this important correction seems to have been overlooked by Professors Hempel and Dennis in the second English edition, although correctly stated in the first.* The tension of aqueous vapor does not affect the *change* of pressure unless there is a change of temperature.

The following figures, of two trial analyses of air kindly made by Mr. Edward Mallinckrodt, Jr., serve to illustrate the method. The minus sign before the second reading signifies that the counterpoise bulb was below the other, almost as far as the level of the floor.

	I.	II.
Difference of water level at first	+100 0 cm.	+100.0 cm.
Difference of water level after absorption of oxygen	−128.0 cm.	−126.5 cm.
Mercury equivalent to first difference	+ 73.3 mm.	+ 73.3 mm.
Mercury equivalent to second difference	− 93.8 mm.	− 92.7 mm.
Total loss of pressure	167.1 mm.	166 0 mm.
Barometer (corrected to 0°)	752.2	752.2
Initial pressure of moist gas = 752.2 + 73.3 mm. =	825.5	825 5
Tension of aqueous vapor ($t^o = 27.6$)	27.4	27.4
Initial pressure of dry gas = ...	798.1	798.1
Percentage of oxygen $= \dfrac{\text{loss of pressure}}{\text{initial dry pressure}} = ..$	20.94	20.80

At another time, Mr. W. N. Stull kindly made another test of the apparatus, finding the following percentages of oxygen in the air of the laboratory : —

$$\frac{100 \times 170.2 \text{ mm.}}{818.0 \text{ mm.}} = 20.80 ; \qquad \frac{100 \times 173.5 \text{ mm.}}{831.8 \text{ mm.}} = 20 \cdot 86 ;$$

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* See page 77 in edition of 1902, and page 69 in edition of 1892 (Macmillan).

$$\frac{100 \times 168.9 \text{ mm.}}{809.7 \text{ mm.}} = 20.86.$$

The mean of all these analyses indicates 20.85 per cent by volume of oxygen in the air of the laboratory, a value which is probably very near the truth.*

It is interesting to note that the difference between the results 20.94 per cent and 20.80 per cent is caused by a difference of reading in the water column of 15 mm. Hence it is clear that a meter-stick, or a rod provided with labels whose distance apart may be measured at leisure, is quite sufficiently accurate as a means of measurement for ordinary purposes.

Attention should be called to several possible errors which must be guarded against in this process.

(1) Either no air should be permitted to remain permanently in the tube connecting the pipette and the measuring bulb, or else the volume of the residual bubble should be suitably corrected, according to circumstances.

(2) None of the absorbing liquid should be run into the measuring bulb; or if by accident some of the absorbing liquid finds its way into this bulb, it should be washed away with pure water, in order that it may not affect the tension of the aqueous vapor.

(3) Care should be taken to allow time for the equalization of the temperature change caused by the compression and expansion of the gas as well as for the running down of adhering water.

(4) The temperature must be kept constant, within 0.05° centigrade, a condition which is easily fulfilled by stirring warmer or cooler water into the open receptacle. If an accurate thermometer is not at hand, a sensitive air thermometer may be improvised for this purpose, — for *change* of temperature must especially be guarded against. The ingenious device suggested by Professor Hempel for this correction serves well.†

Of course all these precautions apply equally to the usual measurement under constant pressure, but they are not always heeded.

Attention may be called also to the fact that neither the constant-volume nor the constant-pressure method necessarily affords the true measure of the volume of the absorbed gas. This would only be true if all gases were perfect gases; as a matter of fact, no accurate measure-

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* The method was tried also by a large class of beginners in gas-analysis with successful results.

† Hempel (translated by Dennis) (1902), page 84.

ments of the actual slight contractions or expansions which take place on mixing gases seem to have been made. These are, however, so small, that for ordinary purposes they may be neglected.

It may be a matter of interest to call attention one by one to the percentage effect of the various probable sources of error in the determination of oxygen in air, supposing in each case that the particular error under consideration is the only one present. The analysis is supposed to be conducted in a room having the atmospheric conditions of 20° temperature and 760 mm. pressure, with the apparatus described above. The error is recorded in percentage of the total volume taken.

(1) Omission of the correction for aqueous vapor   0.4 per cent.
(2) Error of 1 mm. in reading water column . .   0.01   "
(3) Constant error of 1° in thermometer in water-jacket . . . .   0.02   "
(4) Change of 1° in temperature of water-jacket   0.5   "
(5) Constant error of 1 mm. in reading barometer column . . . .   0.02   "
(6) Change of 1 mm. in atmospheric pressure . .   0.13   "
(7) Admission of absorbing liquid into measuring bulb, according to amount { from . . .   0   "
{ to perhaps .   1   "
(8) Maximum error from adhering water, perhaps   0.5   "
(9) Possible error from adiabatic contraction, perhaps   1   "
(10) The retention of a bubble of gas 1 cm. long in the 1 mm. capillary . . . .   0.02   "

That all the significant errors may be sufficiently avoided by reasonably careful work is clear from the actual results; but the enumeration of their widely varying effects may be useful in showing the novice where to employ his precautions. Most of these errors apply equally to any kind of gas-analytical work, but many of them are persistently disregarded in common practice.

If the mixture to be analyzed contains gases easily soluble in water, mercury must of course be employed in the measuring bulb, and a good cathetometer should be used for measuring the changes of pressure. A poor cathetometer is often worse than none.

Summary.

In this paper is described a method of gas-analysis which demands only the simplest apparatus, and yet is capable of yielding results accurate enough for many ordinary purposes. The limitations of this apparatus are compared with those of other gas-analytical methods. In particular the importance of applying the correction for aqueous vapor in all methods which depend upon the measurement of changing pressure in constant volume is emphasized.

It is worthy of remark that this simple method forms a highly instructive exercise in gas-analysis for a class of students in this subject.

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